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(71)Applicant : MATSUSHITA ELECTRIC IND CO LTD

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(72)Inventor : UCHINO HIDEO
OZAKI YOSHIYUKI
MORITA TERUYOSHI

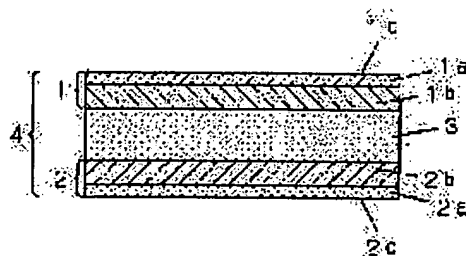
(54) LITHIUM SECONDARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary cell with excellent safety and volume efficiency, with a structure capable of reducing cost, enabled to obtain an optional voltage according to the number of lamination units.

SOLUTION: A structure successively laminating an aluminum current collector 1a, a positive pole binder 1b, a polymer electrolyte layer 3, a negative pole binder layer 2b, and a copper current collector 2a, is formed as one lamination unit. For the cell, enclosing a plurality of the unit lamination units formed by making non-coated surfaces 1c, 2c of the current collectors of the positive pole 1 and negative pole 2 contact with each other inside an outer case, an optional cell voltage is obtained by laminating the lamination units, further, safety is improved and manufacturing cost is reduced.

- 1 正極
- 1a アルミニウム集電体
- 1b 正極合剤層
- 1c 正極集電体未塗布面
- 2 負極
- 2a 銅集電体
- 2b 負極合剤層
- 2c 負極集電体未塗布面
- 3 ポリマー電解質層
- 4 隔電要素



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is a lithium secondary battery which has a laminated structure, and relates to the cell from which the electrical potential difference of arbitration is obtained with the number of unit which carries out especially a laminating.

[0002]

[Description of the Prior Art] In recent years, the request to implementation of the rechargeable battery which development of the large-sized cell for the object for electric vehicles or the Nighttime stationary energy storage is briskly performed from viewpoints, such as a small cell as a power source for a drive of various electronic equipment and an environmental problem, and energy problems, and is more excellent in economical efficiency with the high voltage and a high energy consistency is strong.

[0003] The lithium secondary battery of the cylindrical shape which used the carbon material which lithium content multiple oxides, such as a lithium cobalt multiple oxide and a lithium manganese multiple oxide, are carried out at a positive electrode, and can carry out occlusion emission of the lithium ion at a negative electrode as most promising fuel cell subsystem that fills these requests or an ellipse, and a square shape is already put in practical use. However, in order to use an inflammable solvent as the electrolytic solution, a problem is in safety at the time of incorrect actuation of a device, and abnormality use, and these rechargeable lithium-ion batteries need to equip various security circuits. Moreover, since the high voltage of hundreds of volts is required to an electric vehicle application, many cells are required, and in order to use a cell as a charge collector of the group cell linked to a serial or juxtaposition, there is a problem that the cost of materials increases. Moreover, when it becomes the aggregate, resistance of a cell also has the problem that will become big and the energy which can be taken out decreases. Since volumetric efficiency is not still better in the case of a cylindrical shape, it is disadvantageous for enlargement.

[0004] On the other hand, for example by JP,9-161757,A, JP,9-320636,A, and JP,9-320637,A, the cell of a plate-like laminated structure by which the cell of the laminated structure which carried out the laminating of the plate put between the saccate separator one by one carried out two or more layer laminating of the electrode layered product also for JP,10-284055,A again is proposed noting that it is suitable for a group cell, since the cell of straight angle mold structure has good volumetric efficiency.

[0005] However, by these cells, although volumetric efficiency is improved compared with a cylindrical shape, single cell voltage has the technical problem that it is not what it does not change and can be satisfied in the case of a high-voltage application.

[0006]

[Problem(s) to be Solved by the Invention] This invention solves this technical problem, is excellent in safety and volumetric efficiency, is the structure in which manufacture cost reduction is possible, and offers the cell from which the electrical potential difference of arbitration is obtained with the laminating number of unit.

[0007]

[Means for Solving the Problem] in order to solve the above-mentioned technical problem -- the 1st configuration of this invention -- a positive-electrode charge collector and a positive electrode -- a mixture, a polymer electrolyte, and a negative electrode -- what carried out two or more unit laminating of what carried out the laminating to the order of a mixture and a negative-electrode charge collector as one unit is enclosed in a single sheathing case, and the non-applied fields of a positive-electrode charge collector and a negative-electrode charge collector are contacted mutually.

[0008] moreover, the thing using the metallic foil which the 2nd configuration of this invention becomes from a clad plate as a charge collector of a positive electrode and a negative electrode -- it is -- the positive-electrode charge collector of a clad plate, and a positive electrode -- the negative electrode on a mixture, a polymer electrolyte, and another clad plate side -- what carried out two or more unit laminating of what carried out the laminating to the order of a mixture and the negative-electrode charge collector of this clad plate one by one as one unit is enclosed with a single sheathing case. In this case, since the polymer electrolyte containing the solid-state polymer electrolyte or lithium salt which contained lithium salt as an electrolyte, and an organic solvent is used, there is no fluidity in the electrolyte itself, and without having a common electrolyte, even if each unit is in a single sheathing case, it has been independent, and it can obtain the cell voltage of arbitration by the laminating of two or more numbers of unit with said configuration.

[0009] Since the electrical potential difference which carried out series connection of some cels in spite of the cel which consists of one sheathing case is obtained while being able to simplify a production process by said configuration, a sheathing case can be reduced and reduction-ization of cost is attained as a result.

[0010]

[Embodiment of the Invention] The gestalt of operation of this invention is explained based on drawing. Drawing 1 is the mimetic diagram showing the structure of the generation-of-electrical-energy element which is the gestalt of operation of the electrode for lithium secondary batteries of this invention, between positive-electrode binder layer 1b applied to one side of aluminum charge collector 1a of a positive electrode 1, and negative-electrode binder layer 2b applied to one side of copper charge collector 2a of a negative electrode 2, the polymer electrolyte layer 3 is pinched and the generation-of-electrical-energy element 4 is constituted.

[0011] Drawing 2 is the mimetic diagram of the cell which inserted in the aluminum laminate film pack two or more layered products 5 to which the laminating of the generation-of-electrical-energy element of drawing 1 was carried out one by one where negative-electrode charge collector non-applied side 2c is contacted to positive-electrode charge collector non-applied side 1c. The positive-electrode lead 7 made from aluminum is welded with the positive-electrode lead attachment terminal which prepared 6 in the positive electrode of two or more layered products 5. The negative-electrode lead 9 copper with the negative-electrode lead attachment terminal which prepared 8 in the negative electrode of two or more layered products 5 is welded. 10 -- aluminium foil -- middle -- much more -- ** -- it is the sheathing case which carried out, laminated the polypropylene film in the inside, laminated the polyethylene terephthalate film and the nylon film outside, respectively, and was formed from the unified laminate film. Two or more layered products 5 held in the interior of this sheathing case 10 are in the condition that the positive-electrode lead 7 and the negative-electrode lead 9 were drawn in the exterior of the sheathing case 10, and they secure an airtight and it obturates them by thermal melting arrival etc. in opening of the sheathing case 10.

[0012] Since the cell of the gestalt of this operation is contained by the sheathing case 10 where two or more generation-of-electrical-energy elements 4 which made laminating connection are single to a serial, it can obtain the cell voltage of the arbitration according to the number of the generation-of-electrical-energy elements 4 which carried out the laminating. Moreover, since the case of a cell, an obturation plate, current collection tabs, etc. are reducible compared with the case where the conventional cell is connected to a serial, man day reduction and sharp reduction of ingredient cost are possible.

[0013] Drawing 3 is the mimetic diagram showing the electrode of the laminated structure which used

for the charge collector the clad plate which is the gestalt of other operations of the lithium ion battery of this invention. Positive-electrode binder layer 1b is applied to the front face of the aluminium foil 12 of a clad plate 11, negative-electrode binder layer 2b is applied to the front face of the copper foil 13 of this clad plate 11, and a positive electrode and a negative-electrode combination clad plate are constituted. Among 2 sets of these clad plates, the aforementioned polymer electrolyte layer 3 is pinched and the generation-of-electrical-energy element 14 is constituted.

[0014] Drawing 4 shows the typical sectional view of two or more layered products where the laminating of the generation-of-electrical-energy element of drawing 3 was carried out one by one. a clad plate is sufficient as the both ends 15 of a layered product, i.e., the positive-electrode side edge section, and the negative-electrode side edge section 16 -- carrying out -- one side of aluminium foil and copper foil -- respectively -- a positive electrode -- a mixture and a negative electrode -- what applied the mixture may be used. the case of a clad plate -- a positive-electrode lead -- a negative electrode -- from the copper foil part 13 which has not carried out coating of the mixture -- taking -- a negative-electrode lead -- a positive electrode -- a mixture will be taken from the aluminium foil part 12 which has not carried out coating. When using an aluminium foil charge collector or a copper foil charge collector for an edge, the positive-electrode lead 7 will take non-coating section 1c of the aluminium foil of drawing 1 to the negative-electrode lead 9 from non-coating section 2c of copper foil. Cylinder tubing can be used as a sheathing case 10, using the laminate film pack shown in drawing 2.

[0015] While the cell which carried out the laminating with the gestalt of other operations also has the same effectiveness as the above, a large man day and cost reduction are possible for it from a positive electrode and a negative electrode being connected by the clad plate.

[0016] In addition, when a sheathing object is a metal also in the gestalt of which operation, some of positive electrodes or negative-electrode charge collectors of a layered product are exposed with the metal, and by making it contact, it can also consider as a terminal and does not limit to the structure indicated with said configuration, components, and the quality of the material.

[0017] Moreover, although copper or a nickel metallic foil is desirable as aluminium foil and a negative-electrode charge collector as the quality of the material of said positive-electrode charge collector, it may not limit to especially these and you may be gauze.

[0018] Moreover, although said especially clad plate does not limit and various kinds of approaches used by junction of aluminum and a dissimilar material, such as scorification and a pressure-welding method, can be considered, what is depended on pressure-welding methods, such as hot pressure welding and cold pressure welding, is desirable.

[0019] Said positive-electrode binder layer consists of a polymer containing the nonaqueous electrolyte which dissolved positive active material, an electric conduction agent, lithium salt, or lithium salt.

Although the lithium content multiple oxide which was permuted by the compound of metals other than transition metals, such as a lithium content multiple oxide by which some transition metals in LiMn_2O_4 , LiCoO_2 and LiNiO_2 , or a formula were permuted with other transition metals, such as nickel, Fe, Cr, Ti, and V, or B, aluminum, P, Sn, Si, and semimetal as positive active material, and is shown can be used, it does not limit to especially these. As an electric conduction agent, carbon materials, such as an artificial graphite and acetylene black, are used. The electrolyte salt which contains the solvent and lithium of a non-drainage system which are used for the conventional cell as the electrolytic solution is used. One sort or two sorts or more of solvents chosen from the group which specifically consists of the ether, such as straight chain-like ester, such as cyclic ester, such as ethylene carbonate, propylene carbonate, and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate, 1, 2-dimethoxyethane, and 2-methyl tetrahydrofuran, are used. Moreover, as an electrolyte salt, LiPF_6 , LiBF_4 grade, and mineral salt are used. As a polymer holding the electrolytic solution, polyethylene oxide (henceforth PEO) is used as a matrix, for example.

[0020] Said negative-electrode binder layer consists of a polymer containing the nonaqueous electrolyte which dissolved a negative-electrode active material, an electric conduction agent, lithium salt, or lithium salt. Although compounds, such as a lithium metal, a lithium alloy, oxide that carries out occlusion emission of the lithium, and a CHITSU ghost, a carbon material, etc. are raised as said

negative-electrode active material, a lithium metal, a lithium alloy, etc. which are the large dissolution mold electrode of the formation of a form status change have the most desirable carbon material preferably also in compounds, such as oxide and a CHITSU ghost, or a carbon material. In addition, as a polymer holding an electric conduction agent, the electrolytic solution, and the electrolytic solution, what is used with said positive electrode is usable.

[0021] As said polymer electrolyte, it is used as the solid-state polymer electrolyte only containing lithium salt, or a gel electrolyte which made the electrolytic solution contain. As an ingredient of a polymer electrolyte, polymers, such as a polymer electrolyte which graft-ized ionic dissociation radicals, such as matrices of complex, such as PEO, polypropylene oxide (henceforth PPO), a polyacrylonitrile, a polyvinyl pyrrolidone, a polyvinyl chloride, and polyvinylidene fluoride, these isocyanate bridge formation objects, or low molecular weight PEO and PPO, to the polymer principal chain, FENIN oxide, and a FENIN sulfide system polymer, can be used.

[0022] As said sheathing case, the complex or metal can which laminated thermal melting arrival nature resin is used on a metal. Alloys, such as metals, such as aluminum, iron, copper, nickel, and titanium, stainless steel, and an aluminium alloy, can be used for the sheathing metal of lamination complex. As thermal melting arrival nature resin of lamination complex, high polymer films, such as polyethylene, polypropylene, and a polyvinyl chloride, can be used. Moreover, aluminum, iron, stainless steel, etc. can be used as a metal can.

[0023]

[Example] Hereafter, this invention is not limited by these examples although the example of this invention is explained concretely.

[0024] (Example 1) First, carried out the 6 phosphorus-fluoride acid lithium dissolution at the mixed solvent which mixed ethylene carbonate and propylene carbonate by the volume ratio 1:1, polyethylene oxide was made to contain the electrolytic solution of concentration 1.5M, and the polymer gel electrolyte was produced to it. this -- as the powder of a lithium manganese multiple oxide (LiMn_2O_4), and carbon black -- acetylene black -- the weight ratio 10:80:10 -- comparatively -- coming out -- mixing -- a positive electrode -- a mixture -- the paste was produced, this was applied to one side of aluminium foil with a thickness of 20 micrometers, it dried, and the positive-electrode sheet was produced.

[0025] next, said polymer gel electrolyte and an artificial graphite -- the weight ratio 22:78 -- comparatively -- coming out -- mixing -- a negative electrode -- a mixture -- the paste was produced, this was applied to one side of copper foil with a thickness of 18 micrometers, it dried, and the negative-electrode sheet was produced.

[0026] Then, to said polymer gel electrolyte, the film was formed by application, room temperature neglect desiccation was carried out, and the sheet-like polymer electrolyte layer was produced.

[0027] Subsequently, the piece of a sheet of a dimension the angle of 15cm was taken out from the said sheet-like positive-electrode, sheet-like negative-electrode, and sheet-like gel polymer electrolyte layer. Between this piece of a positive-electrode sheet, and the piece of a negative-electrode sheet, it intervened, the laminating of the piece of a polymer electrolyte layer sheet was carried out, and the generation-of-electrical-energy element was produced. The laminating of this generation-of-electrical-energy element was carried out to the two-piece serial, it considered as the two-layer structure layered product, and the current collection lead was attached in the edge of the positive electrode of this layered product, and each negative electrode by spot welding. Moreover, it connected electrically by the caulking between each generation-of-electrical-energy element.

[0028] Subsequently, it inserted in the aluminum laminate film which made this layered product saccate, and decompressing, where a terminal is drawn from a positive electrode and a negative electrode outside, respectively, it obturated, and thermal melting arrival was carried out and the layer built cell of the two-layer structure was obtained.

[0029] This cell was made into charge and discharge current consistency 0.5 mA/cm², it discharged to charge termination electrical-potential-difference 8.6V and discharge-final-voltage 6.0V, and 10 cycle deed and the average electrical potential difference of 10 cycle eye obtained 7.6V and positive-electrode

capacity consistency 110 mAh/g for this.

[0030] (Example 2) The piece of a clad plate of the aluminum with a thickness of 0.05mm and the copper with a thickness of 0.05mm which were joined by cold pressure welding was started as a disc-like thing with a diameter of 15mm, and this was made into the charge collector of a positive electrode and a negative electrode.

[0031] first, the aluminum side of said piece of a clad plate -- the positive electrode of an example 1 -- a mixture -- a copper surface -- a negative electrode -- the mixture was applied and the clad two-poles plate electrode which has the binder layer from which a polarity differs on both sides was produced. next, the aluminum foil surface of said clad plate -- the positive electrode of an example 1 -- the mixture was applied and the clad positive-electrode plate to which the spreading side and the copper surface of the opposite side were exposed was produced. moreover, this -- reverse -- the copper-foil face of said clad plate -- the negative electrode of an example 1 -- the mixture was applied and the clad negative-electrode plate to which the spreading side and the aluminum side of the opposite side were exposed was produced.

[0032] Then, between a clad positive-electrode plate and the first clad two-poles plate, between the first and the second clad two-poles plate, said sheet-like polymer electrolyte was inserted between the second clad two-poles plate and a clad negative-electrode plate, and it considered as the 3 layer-structure layered product. The copper negative-electrode obturation plate was attached in the aluminum side of a negative-electrode clad plate for the positive-electrode obturation plate made from aluminum at the copper surface of the clad positive-electrode plate of this layered product, and this was inserted in the insulating tube made from polyethylene, and the obturation plate was equipped with the gasket, it inserted in the cylinder made from stainless steel, opening was obturated, and the cylindrical shape cell was obtained. Although the aluminum and copper which are usually used with the nonaqueous electrolyte rechargeable battery were used in this example as the quality of the material of a positive-electrode obturation plate and a negative-electrode obturation plate, neither may not be a metal, as long as it is not limited to aluminum and copper, and it can also use various kinds of metals, such as nickel, iron, titanium, and stainless steel, and there is conductivity, especially since the electrolyte does not touch in this case. This cell was made into charge and discharge current consistency 0.5 mA/cm², it discharged to charge termination electrical-potential-difference 12.9V and discharge-final-voltage 9.0V, and 10 cycle deed and the average electrical potential difference obtained 11.4V and positive-electrode capacity consistency 110 mAh/g for this.

[0033] (Example 3) Between the sheet-like positive electrode of an example 1, and the first clad two-poles plate of an example 2, said sheet-like polymer electrolyte was inserted between between the first and the second and third clad two-poles plate, the third clad two-poles plate, and the sheet-like negative electrode of an example 1, and it considered as the 4 layer-structure layered product. The current collection terminal of a positive electrode and a negative electrode was attached like the example 1, it inserted and obturated in the aluminum laminate film pack, and the cell of a four-layer laminated structure was obtained.

[0034] When this cell was made into 0.5 mA/cm² and the charge and discharge current consistency was evaluated, it discharged to charge termination electrical-potential-difference 17.2V and discharge-final-voltage 12V, and 10 cycle deed and the average electrical potential difference obtained 15.2V for this.

[0035] (Example 4) The layer built cell of 5 layer structures was obtained by the same approach as an example 1 except using a nickel foil with a thickness of 15 micrometers as a negative-electrode charge collector.

[0036] When this cell was made into 0.5 mA/cm², the charge and discharge current consistency was evaluated and it discharged to charge termination electrical-potential-difference 21.5V and discharge-final-voltage 15V, the average electrical potential difference obtained 19.0V.

[0037] In addition, although the aluminum laminate film was used as a sheathing case in the examples 1, 3, and 4, even if it uses the laminate film of other metals, the same property as said example can be acquired.

[0038] Moreover, in the example 2, although the stainless steel can was used, even if it uses other metal

cans, the same property as said example can be acquired.

[0039] Moreover, in the example 2, as the quality of the material of a positive-electrode obturation plate and a negative-electrode obturation plate, although the aluminum and copper which are usually used with the nonaqueous electrolyte rechargeable battery were used, neither may not be a metal, respectively, as long as it is not limited to aluminum and copper, and it can also use various kinds of metals, such as nickel, iron, titanium, and stainless steel, and there is conductivity, especially since the electrolyte does not touch in this case.

[0040]

[Effect of the Invention] as mentioned above, a positive-electrode charge collector and a positive electrode -- a mixture, a polymer electrolyte, and a negative electrode -- the cell which enclosed with the single sheathing case two or more unit layered product to which the non-applied field of a positive-electrode charge collector and the non-applied field of a negative-electrode charge collector were mutually contacted by making into one unit what carried out the laminating to the order of a mixture and a negative-electrode charge collector -- or Two or more unit layered product which intervened the polymer electrolyte and carried out two or more laminatings of what used for the charge collector the metallic foil which consists of a clad plate, applied positive active material to the one front face, and applied the negative-electrode active material to other front faces one by one as one unit by the cell enclosed with the single sheathing case The cell voltage of arbitration can obtain by the laminating of two or more units. Moreover, since simplification of a process is possible, manufacture cost reduction is possible.

[Translation done.]